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Reaction of Electronically Excited O₂ with CO

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Reaction of Electronically Excited O₂ with CO

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Photolysis of solutions of O₂ in CO at 77°K with 2537-Å radiation has been found to produce O₃ and CO₂. Absorption of radiation in this wavelength region by O₂ corresponds to the forbidden transition $^3\Sigma_u^- \leftarrow ^3\Sigma_g^-$, the Herzberg bands of O₂. Since O₂ but not CO absorbs 2537-Å radiation and since O₂ cannot dissociate directly, the reaction must occur between excited O₂ and CO. The quantum yield for O₃ formation in the limit of low O₂ concentration is of the order of 0.33 and increases slightly with increasing O₂. In the concentration range studied CO₂ is formed somewhat faster than O₃. These results suggest that an intermediate is involved in the reaction which is capable of direct reaction with CO and O₂ to form products. This intermediate is proposed to be CO₃^{*}, and a mechanism involving this species is postulated.

Author

INTRODUCTION

MOST photochemical reactions of O₂ involve production of an excited O₂^{*} which immediately dissociates so that atomic oxygen becomes the actual reactive species in any subsequent reactions which may occur. However, if the rate of dissociation of O₂^{*} is

of O₂¹ and in the photochemical production of O₃ at 1849 Å² and 2537 Å.³

In the present paper we wish to report definite evidence for the reaction of electronically excited O₂ with CO to produce O₃ and CO₂. The experiments for the most part involve photolysis of liquid mixtures of O₂ and CO at 77°K with 2537 Å radiation. Since the einstein at 2537 Å is 112 kcal and the dissociation

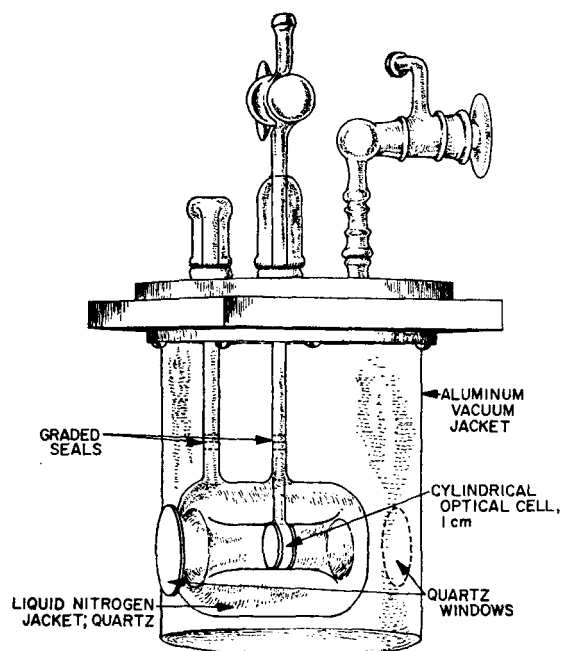


FIG. 1. Low-temperature cell.

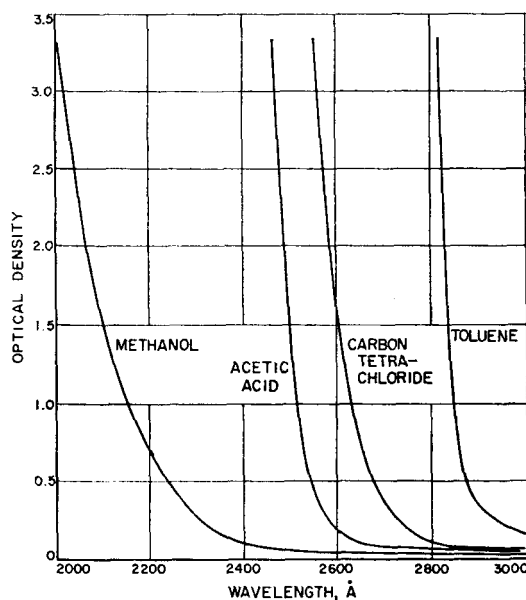


FIG. 2. Optical densities of liquids used for filters.

slow, as in the case where there is an energy deficiency or where a rate determining intersystem crossing is required, the possibility of direct reaction of O₂^{*} must be considered. No well-defined example of an electronically excited O₂ reaction has been reported, although the possibility of such processes has been discussed in connection with the mercury-photosensitized reactions

energy of O₂ 118 kcal/mole, production of atomic oxygen in the initial photochemical step can be ruled out.

EXPERIMENTAL

The cell used for photolyzing the solutions is shown in Fig. 1. It consists of a 1-cm optical cell surrounded

¹ See, for example, E. K. Gill and K. J. Laidler, Can. J. Chem. **36**, 79 (1958).

² W. B. DeMore and O. Raper, Can. J. Chem. **41**, 808 (1963).

³ S. W. Benson, *Ozone Chemistry and Technology* (American Chemical Society, Washington, D. C., 1959), p. 405.

TABLE I. Determination of the CO₂ yield from the photolysis of CO-O₂ solutions.

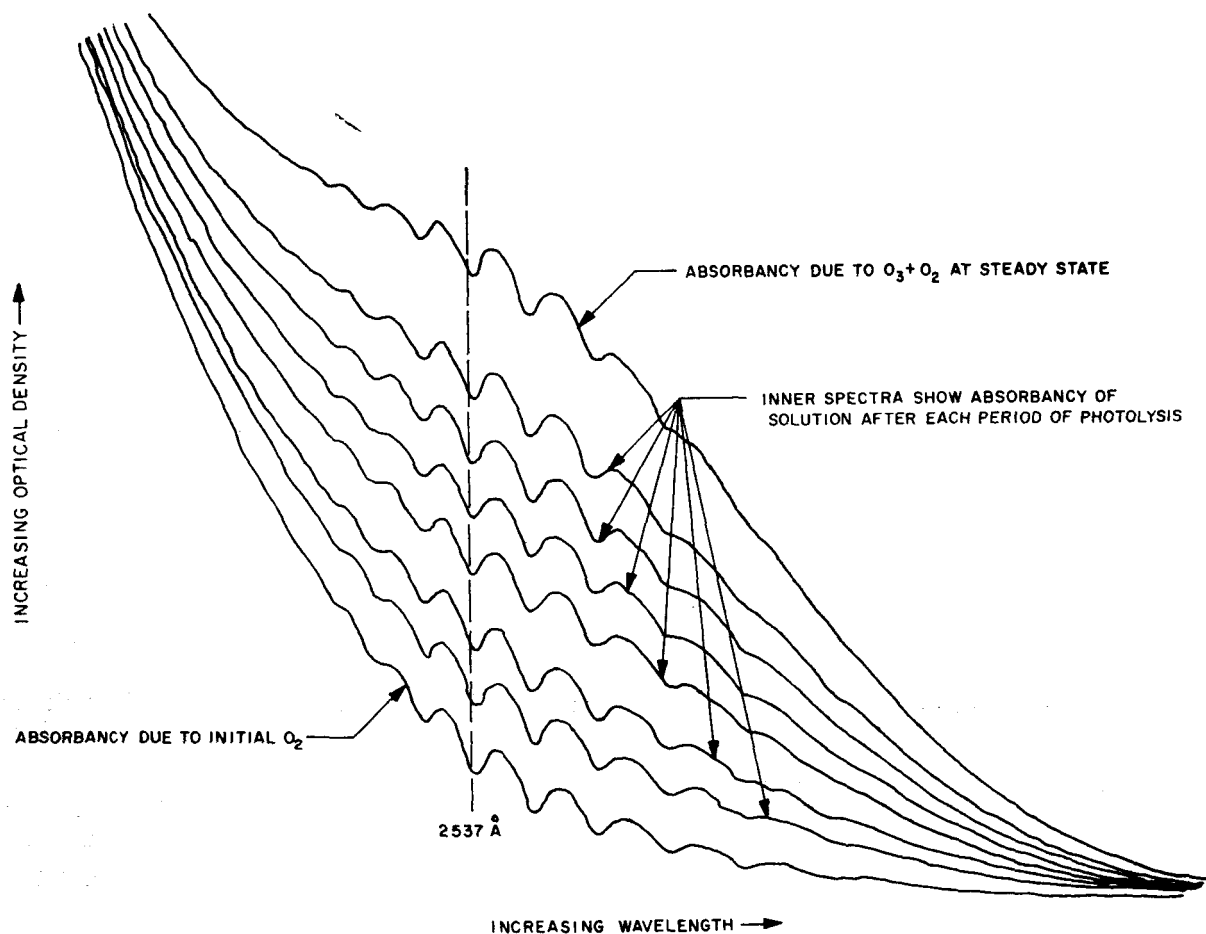
1	2	3	4	5	6
Mole ratio O ₂ /CO	Photolysis time at 2537 Å (min)	Total O ₂ produced (and decomposed) (moles×10 ⁶)	Total CO ₂ recovered (moles×10 ⁶)	CO ₂ produced as a result of O ₂ absorption (moles×10 ⁶)	Ratio of Column 5 to Column 3
0.1312 ^a	...	2.36 ^a	2.38 ^a	...	1.01 ^a
0.0573	14	1.79	3.91	2.12	1.18
0.0970	180	13.5	30.2	16.7	1.24
0.1047	6	1.27	2.83	1.56	1.23
0.1682	210	14.4	31.3	16.9	1.17

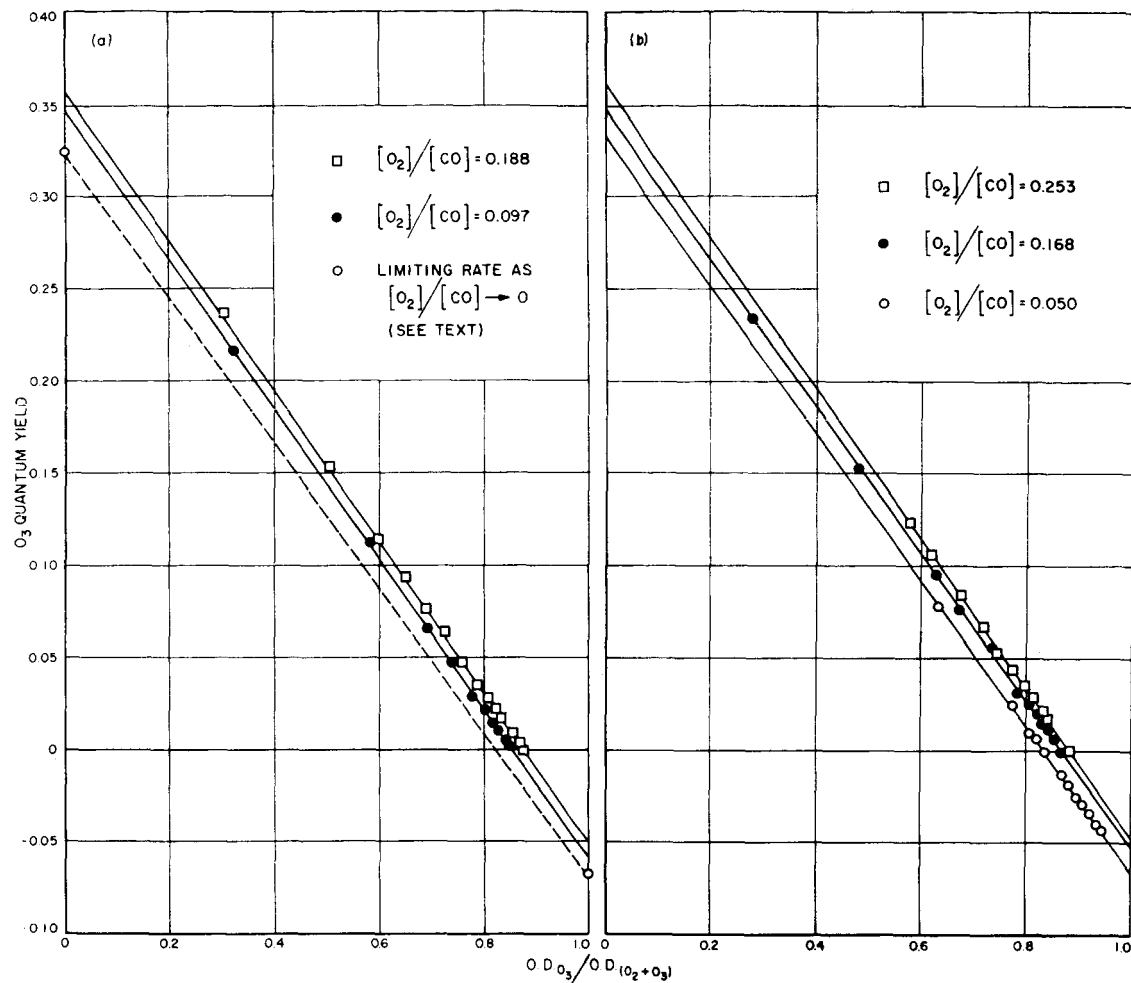
^a Special run (see text).

by a liquid-nitrogen reservoir in such a manner as to leave the optical path free while providing cooling for the solution. The cell and reservoir are suspended in an evacuated aluminum jacket with quartz windows designed to fit in a Cary uv spectrophotometer.

As a source of 2537-Å radiation a low-pressure mercury arc was used which was of conventional design save for a tight flat coil which concentrated the light

in the region of the aperture. A 1-cm-by-50-mm diameter quartz optical cell filled with methanol was used to filter out radiation of $\lambda < 2000$ Å. In those runs where complete photolysis of the O₃ in the solution was necessary, a B-H6 high-pressure mercury arc was used in conjunction with a toluene filter. Complete photolysis of the O₃ was possible under these conditions since the light transmitted by the toluene was

FIG. 3. Spectra produced by O₂ and O₃ in a typical run.

FIG. 4. Results of several runs at different O₂/CO ratios.

absorbed by the O₃ but not by the O₂ in the concentrations used, thus preventing reformation of O₃ by the O₂-CO photochemical reaction. The optical densities of all the filters used during the course of the experiments are shown in Fig. 2.

The gases used were Linde tank oxygen and Matheson cp carbon monoxide. Each gas was passed through a Drierite-Ascarite train and distilled once from the liquid before it was condensed in the cell. In those runs where O₃ was added initially, it was prepared by a tesla coil discharge in O₂, and twice distilled from liquid argon before use.

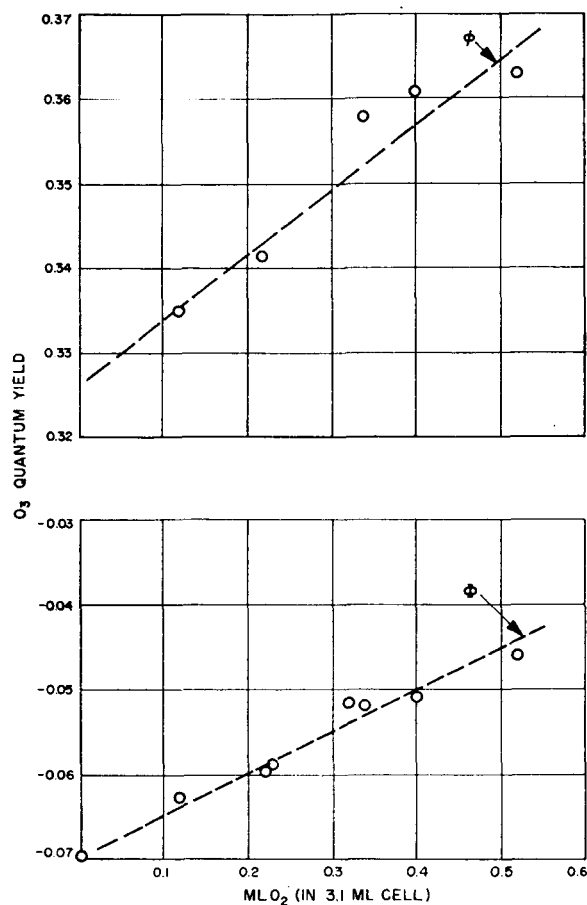
Runs were made by condensing measured amounts of O₂ and CO in the cell and determining the initial optical density on the Cary. The solutions were then irradiated for short periods of time and the optical density was measured after each period (see Fig. 3). It was necessary to increase the photolysis periods as the O₃ approached its steady-state concentration. The runs with added O₃ were similar except that the initial O₃ concentration was higher than the steady-state concentration and the rate of photolysis was followed

down to steady-state conditions. All of the O₃ was then decomposed as described above, after which the rate of formation back to the steady state was followed. The runs used to determine the total CO₂ yield were similar to all others except that the total irradiation time was varied and all of the O₃ was decomposed prior to recovering the CO₂. CO₂ was recovered by pumping off the CO and O₂ to a good vacuum and then transferring the CO₂ to a U-tube. The CO₂ was kept at liquid-nitrogen temperature and the U-tube was sealed off while pumping. The CO₂ concentration was then determined either manometrically or by mass spectrometry. The O₃ concentration, in all cases, was determined spectrophotometrically in solution using an extinction coefficient of 3030 liter mole⁻¹·cm⁻¹ at 2550 Å.⁴ The actinometry for all runs was done in the same manner as that described in the following paper.⁵

In a final group of experiments, N₂-O₂ solutions

⁴ W. B. DeMore and O. Raper, "Hartley Band Extinction Coefficients of O₃ in the Gas Phase and in Liquid N₂, CO, and Argon," J. Phys. Chem. (to be published).

⁵ W. B. DeMore and O. F. Raper, J. Chem. Phys. **40**, 1053 (1964).

FIG. 5. Effect of added O_2 on ϕ and Φ .

were photolyzed in the same manner as those containing CO and O_2 . Irradiation of these solutions for extended periods failed to produce O_3 sufficient to detect on the Cary. In addition, CO- O_2 solutions were photolyzed through the acetic acid and carbon tetrachloride filters whose optical characteristics are shown in Fig. 2, and, in each case, some O_3 was produced.

RESULTS

Since O_3 is being formed and decomposed simultaneously by the absorption of 2537-Å radiation by O_2 and O_3 , the total rate for O_3 formation must be the resultant of these two separate processes. The individual rates for formation and decomposition in turn depend on the total light absorbed by the solutions as well as on the fraction of light absorbed by O_2 and O_3 . Expressing these fractions in terms of optical densities, the over-all rate for O_3 formation can be written as follows:

$$\frac{d(O_3)}{dt} = \left[\frac{OD_{O_2}}{OD_{(O_2+O_3)}} \phi - \frac{OD_{O_3}}{OD_{(O_2+O_3)}} \Phi \right] I_{abs}. \quad (A)$$

In this expression ϕ represents the quantum yield for O_3 formation from O_2 at 2537 Å and Φ the quantum

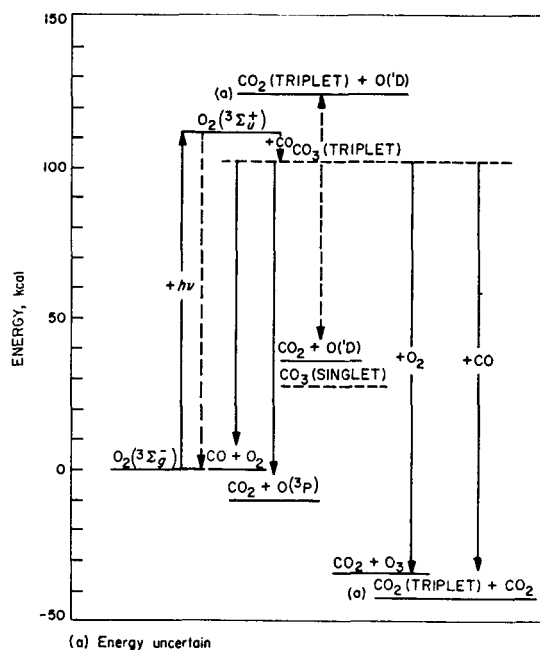
yield for O_3 decomposition at the same wavelength. Substituting R for $d(O_3)/dt$ and f for $OD_{O_3}/OD_{(O_2+O_3)}$, this equation can be rearranged to

$$R/I_{abs} = \phi - f(\phi + \Phi). \quad (B)$$

A plot of R/I_{abs} , which represents the over-all quantum yield, vs f should therefore yield a straight line with intercepts $f=0$ and $f=1$ equal to ϕ and Φ , respectively. In addition, the results of separate runs at different O_2/CO ratios would show what effect, if any, the O_2 concentration has on the individual quantum yields.

Figures 4(a) and (b) show the results of several such runs at different O_2/CO ratios. The straight lines obtained in these plots tend to confirm the relationship between ϕ and Φ predicted by Eq. (B), and the change in the intercepts with changing O_2/CO ratio indicates that both ϕ and Φ are dependent on the O_2 concentration. The effects on ϕ and Φ are shown in Fig. 5. The limiting values of these two quantities as O_2 goes to zero are represented by the lower curve in Fig. 4(a).

The results from those runs in which the CO_2 yield was measured are shown in Table I. The first run shown in the table lists the results obtained by photolyzing a CO- O_2 - O_3 solution under those conditions mentioned above where O_2 does not absorb and the CO- O_2 photochemical reaction is avoided. This run indicates that photolysis of O_3 in these solutions produces CO_2 in an amount equivalent to the O_3 decomposed, which is in agreement with other recent work by the authors on the photolysis of O_3 -CO solutions.⁵



(a) Energy uncertain

FIG. 6. Spin and energy considerations in proposed mechanism.

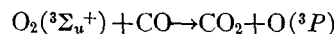
For the remaining runs in the table, the first two columns show the O₂/CO mole ratios and the total photolysis times used. With the knowledge of ϕ , Φ , and I_{abs} in each solution the total amount of O₃ formed and, subsequently, decomposed was calculated graphically and these figures are shown in Column 3. Column 4 shows the total amount of CO₂ recovered at the end of each run. Since the first run shown in the table indicates that an amount of CO₂ equal to that of O₃ is to be expected from O₃ photolysis, Column 5 is the difference between Columns 3 and 4 and represents the CO₂ produced other than as a consequence of O₃ photolysis, i.e., as a result of the absorption of light by O₂. Column 6 shows the ratio of Column 5 to Column 3 and indicates that CO₂ is formed at a rate some 17 to 24% faster than is O₃ in these solutions. The spread in these results is within the limit of error of the determinations, since any error in Column 3 or 4 will be doubled in Column 6.

DISCUSSION

The results of this investigation prove that CO can react directly with electronically excited O₂ to produce O₃ and CO₂. Direct dissociation of O₂ in these solutions is ruled out, since the energy of the quantum at 2537 Å is insufficient to break the O₂ bond. Direct reaction between O₂ and O₂* to give O₃ and O(³P) can also be ruled out for several reasons: (1) N₂-O₂ solutions photolyzed under identical conditions in the present work produced no O₃, nor was any produced by photolysis of pure liquid O₂ under similar conditions⁶; (2) ground-state oxygen atoms have been shown to be unreactive with CO under these conditions,⁷ and an oxygen atom mechanism would therefore not explain the simultaneous formation of CO₂ and O₃; (3) such a direct dependence on the O₂ concentration is not consistent with the O₂ dependence observed (see Fig. 5). The argument presented in (2) can be used to rule out any mechanism which requires that the initial formation of CO₂ occurs by an atomic oxygen mechanism. The CO₂ which is formed by subsequent photolysis of O₃ results from a reaction between O(¹D) and CO, and this subject, together with the effect of O₂ on Φ , will be discussed in greater detail elsewhere.⁵

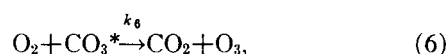
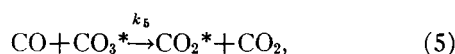
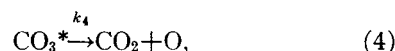
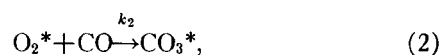
The absorption of light in the region from 2400 to 3000-Å by O₂ probably leads to the ³Σ_u⁺←³Σ_g⁻ transition,⁸ although there is some evidence that the transition may be more complex in the liquid phase.⁹ Assuming the ³Σ_u⁺ state is the O₂ state involved, the over-all

reaction



is consistent with spin conservation rules and is exothermic by at least 112 kcal. Production of O(³P) in this system is equivalent to O₃ formation, since O(³P) cannot react with CO and must eventually undergo reaction with O₂ to form O₃. Since this reaction is exothermic by 25 kcal, CO₂ and O₃ are produced in this system from ground-state O₂ and CO with a net gain of 34 kcal/mole.

While the reaction above represents the over-all process occurring in these solutions, it does not explain the dependence of ϕ on the O₂ concentration shown by Fig. 5, nor does it explain the slight excess of CO₂ over O₃ which is observed. A satisfactory explanation for all the results reported can be given, however, if CO₃* is postulated as an intermediate in the reaction. The results will therefore be discussed in terms of the following mechanism:



In Reaction (1), C is used to indicate that fraction of O₂* formed which subsequently reacts with CO to form CO₃*. If every O₂* undergoes this reaction, C is equal to 1, but if other deactivation processes are occurring in the solution C becomes proportionately smaller. The information obtained from the present experiments is insufficient for evaluating C, but since the transition from O₂(³Σ_u⁺) to the ground state is forbidden the O₂* may have a long lifetime and the probability of reaction with CO may therefore be quite high. Under these circumstances C would be close to 1 and Reaction (3) would represent the primary path for deactivation of O₂*. It should be pointed out also that C is constant only so long as the solution conditions remain constant. This presents no serious limitations in the present experiments since only minor concentration changes were made in the solutions.

If steady-state conditions are assumed for O₂* and CO₃* in Reactions (1) through (6), the following expressions can be written for the O₃ quantum yield ϕ

⁶ E. Briner, Ref. 3, p. 1.

⁷ W. DeMore and O. F. Raper, JPL Space Programs Summary No. 37-17, Vol. IV.

⁸ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1959), p. 276.

⁹ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1959), p. 280.

and the CO₂ quantum yield ϕ_{CO_2} :

$$\phi = C \left[\frac{k_4 + k_6(\text{O}_2)}{k_3 + k_4 + k_5(\text{CO}) + k_6(\text{O}_2)} \right], \quad (\text{C})$$

$$\phi_{\text{CO}_2} = C \left[\frac{k_4 + 2k_5(\text{CO}) + k_6(\text{O}_2)}{k_3 + k_4 + k_5(\text{CO}) + k_6(\text{O}_2)} \right], \quad (\text{D})$$

and the ratio of the CO₂ to O₃ quantum yield is given by

$$\phi_{\text{CO}_2}/\phi = 1 + 2k_5(\text{CO})/[k_4 + k_6(\text{O}_2)]. \quad (\text{E})$$

The extrapolation to zero O₂ concentration shown in Fig. 5 gives an O₃ quantum yield of 0.326. From the increase in ϕ with added O₂ it can be shown using the expression for ϕ in Eq. (C) that $k_6(\text{O}_2)$ is not greater than one tenth k_4 at the highest O₂ concentration used. If $k_6(\text{O}_2)$ is then neglected in Eq. (E), the experimental value of 1.2 found for this ratio indicates that $k_5(\text{CO})$ is also of the order of one-tenth k_4 . The value 0.326 therefore represents to a first approximation the ratio $Ck_4/(k_3+k_4)$, as well as a lower limit for C (for $k_3=0$). In the more likely case where C is near unity, the value of k_3 is approximately twice that of k_4 .

Some of the energy and spin considerations involved in the present work are represented graphically in Fig. 6. The heavy black arrows represent the reactions in-

volved in the proposed mechanism, while the dotted arrows show other possible but less probable reactions. As this figure shows, most of the other reaction paths available in the system are either energetically unfavorable or violate spin conservation rules.

The singlet CO₃ shown in Fig. 6 represents that postulated by Katakis and Taube in their recent studies of exchange between O(¹D) and CO₂.¹⁰ They proposed that at high pressures the reaction O(¹D) + CO₂ + M → CO₃ + M occurs which presumably gives a singlet CO₃. The CO₃* proposed here can be represented as an excited triplet state of the same molecule.

One other interesting aspect of the present work is that it serves to explain the results obtained by McNesby in his studies of the photolysis of CO-O₂ solutions with a low-pressure mercury arc.¹¹ Since the 2537-Å line is far more intense than the 1849-Å line in these arcs, the reaction described here was undoubtedly predominant in his system and probably accounts for the large CO₂ yields which were observed.

ACKNOWLEDGMENTS

The authors are greatly indebted to Dr. Hadley Ford and Professor Sidney Benson for many helpful discussions throughout the course of this work.

¹⁰ D. Katakis and H. Taube, J. Chem. Phys. **36**, 416 (1962).

¹¹ J. R. McNesby, J. Chem. Phys. **31**, 283 (1959).